

# Coupling Aggressive Mass Removal with Microbial Reductive Dechlorination for Remediation of DNAPL Source Zones—A Review and Assessment

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### **Keywords**

aquifer, remediation, bioremediation, post-treatment, source-zone, DNAPL, reductive dechlorination, physical-chemical, innovative technologies, microbial degradation

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### **Nomenclature & Acronyms**

$r$	spill radius
$h$	spill depth
$S_o^{AVG}$	average NAPL saturation
$n$	porosity
$\rho_{PCE}$	PCE density
$C_{aq}^{PCE}$	aqueous phase PCE concentration
$V_d$	pore water velocity
$L_p$	NAPL pool length
$\alpha_v$	vertical dispersivity
$D_{aq}^{PCE}$	PCE bulk aqueous phase diffusion coefficient

AATDF: Advanced Applied Technology Demonstration Facility

CMC: critical micelle concentration

*cis*-DCE: *cis*-1,2-dichloroethene

DNAPL: dense non-aqueous phase liquid

GTP: ganglia-to-pool ratio

HCB: hexachlorobenzene

HGP: high ganglia-to-pool ratio

IGP: infinite ganglia-to-pool ratio

ISCO: in situ chemical oxidation

LGP: low ganglia-to-pool ratio

LNAPL: light non-aqueous phase liquid

NAPL: non-aqueous phase liquid

NRC: National Research Council

O&M: operational and maintenance

PCE: tetrachloroethene

SCRD: State Coalition for Remediation of Drycleaners

SEAR: surfactant enhanced aquifer remediation

TCE: trichloroethene

TEAP: terminal electron accepting process

VC: vinyl chloride  
ZGP: zero ganglia-to-pool ratio

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## **Abstract**

The infiltration of dense non-aqueous phase liquids (DNAPLs) into the saturated subsurface typically produces a highly contaminated zone that serves as a long-term source of dissolved-phase groundwater contamination. Applications of aggressive physical-chemical technologies to such source zones may remove greater than 90% of the contaminant mass under favorable conditions. The remaining contaminant mass, however, can create a rebounding of aqueous-phase concentrations within the treated zone. Stimulation of microbial reductive dechlorination within the source-zone following aggressive mass removal has recently been proposed as a promising staged-treatment remediation technology for transforming the remaining contaminant mass. This work reviews available laboratory and field evidence that supports the development of a treatment strategy that combines aggressive source-zone removal technologies with subsequent promotion of sustained microbial reductive dechlorination. Physical-chemical source-zone treatment technologies compatible with post-treatment stimulation of microbial activity are identified, and studies examining the requirements and controls (i.e., limits) of reductive dechlorination of chlorinated ethenes are investigated. Illustrative calculations are presented to explore the potential effects of source-zone management alternatives. Results suggest that, for the favorable conditions assumed in these calculations (i.e., statistical homogeneity of aquifer properties, known source-zone DNAPL distribution, and successful bioenhancement in the source-zone), source longevity may be reduced by as much as an order-of-magnitude when physical-chemical source-zone treatment is coupled with reductive dechlorination.

## Introduction

Wide-spread use of chlorinated solvents in dry cleaning and metal degreasing operations over the last century resulted in extensive groundwater contamination by compounds such as tetrachloroethene (PCE) and trichloroethene (TCE). When released into the subsurface as dense nonaqueous phase liquids (DNAPLs), chlorinated solvents tend to migrate downward through the unsaturated zone, and can penetrate the water table due to their higher density (Mercer and Cohen 1990). During DNAPL migration, hysteretic capillary forces cause retention of a portion of the liquid within the pores as discontinuous globules or ganglia (EPA 1990; Lenhard et al. 1989; Schwille 1988). Substantial DNAPL volumes can also be retained due to the presence of nonuniform soil texture, which may result in DNAPL pooling (i.e., zones of DNAPL at much higher saturation) above layers or lenses of lower-permeability media (Dekker and Abriola 2000; Essaid and Hess 1993; Saenton et al. 2002; Schwille 1988;). The resulting distribution of DNAPL is, thus, typically complex and non-uniform (Figure 1). Entrapped DNAPL mass tends to dissolve slowly into flowing water, serving as a long-term source of groundwater contamination (Mackay and Cherry 1989; Schwille 1988). The implementation of conventional pump-and-treat remediation for such DNAPL source zones has been ineffective in reducing contaminant concentrations to regulatory endpoints in acceptable time frames (EPA 1996; MacDonald and Kavanaugh 1994; Travis and Doty 1990)

A number of innovative technologies have been developed to enhance contaminant removal from DNAPL source zones (NRC 1994, 1997, 1999). Although these technologies are capable of substantial mass removal under favorable conditions, some DNAPL will likely remain within the porous medium even when treatment is most effective (Fountain et al. 1995; Sale and McWhorter 2001). This remaining contaminant mass can continue to serve as a source of down-gradient contamination, and thus further source-zone treatment or containment may be required. Despite a number of successful field-scale demonstrations of aggressive source-zone treatment technologies, skepticism and concern remains that application of such technologies may not substantially reduce risk

and could potentially worsen site conditions (e.g., through mobilization and redistribution of DNAPL, enhanced transport of metals, elimination of microbial activity, or increased aqueous-phase concentration of contaminants following treatment) (Cherry et al. 1997; Oostrom et al. 1999). From this perspective, some authors have suggested that source containment (i.e., treatment or mitigation of down-gradient contamination emanating from DNAPL sourcezones) is preferable to aggressive physical-chemical source-zone treatment (Cherry et al. 1997; Freeze 2000; Freeze and McWhorter 1997; Kent and Mosquera 2001).

Freeze (2000) advocates a new remediation paradigm in which only source containment is implemented due to the technical impracticability of removing sufficient DNAPL mass to reduce contaminant concentrations to drinking water standards. In contrast, guidelines put forth by the Interstate Technology and Regulatory Cooperation (ITRC) work group, a team comprised of state and federal regulators, call for aggressive source-zone remediation (Jackson 2001). The latter recommendation is based in part on the contention that mass removal from a source zone, even if incomplete, will result in (1) a reduction in mass flux, (2) a reduction in source longevity, (3) a reduction in risk, and (4) a potential enhancement in post-treatment biodegradation (Jawitz et al. 2000; Londergan et al. 2001; Martel et al. 1998; Rao et al. 2002; Yang and McCarty 2003). Recent analytical and numerical modeling investigations suggest that partial source-zone removal may result in significant (several orders-of-magnitude) reductions in post-treatment contaminant mass flux (Lemke and Abriola 2003; Rao et al. 2002; Rao and Jawitz 2003). While a reduction in mass flux may not eliminate the need for further treatment, it could reduce concentrations to levels where microbial transformation of the dissolved phase chlorinated solvents becomes feasible (Adamson et al. 2003; Nielsen and Keasling 1999; Sung et al. 2003; Yang and McCarty 2000). Biostimulation of source-zone microbial dechlorination activity may achieve attenuation of contaminant mass flux to levels that achieve regulatory compliance (i.e., a flux averaged concentration) at a down-gradient well.

Thus, combination of physical-chemical source-zone treatment and post-treatment bioremediation may be an attractive remediation alternative, resulting in reduced source longevity and contaminant mass flux (de Blanc et al. 1997; Rao et al. 2002; Zoller 1998; Zoller and Rubin 2001). Coupling a physical-chemical remediation process that removes significant contaminant mass with a bioremediation “polishing step” to control the contaminant mass flux emanating from remaining DNAPL may provide a synergism that cannot be obtained with existing remediation strategies. Such a staged treatment approach could leverage initial high removal efficiencies of physical-chemical source-zone treatment methods to minimize time to site closure. This sequential treatment approach should not be confused with natural attenuation, a remediation approach that is generally associated with bioremediation of low contaminant concentrations in a groundwater plume (Wiedemeier et al. 1999), nor should it be confused with the recent work on source-zone bioremediation, which relies solely on biotic processes to transform source-zone contamination (e.g., Adamson et al. 2003).

Observations from longer term monitoring at sites where innovative flushing technologies have been implemented suggest that tailoring physical-chemical treatment to enhance post-treatment bioremediation efforts is feasible (Abriola et al. 2003; Mravik et al. 2003; Ramsburg et al. submitted-b). Application of such a staged treatment methodology, however, would require a thorough understanding of both physical-chemical treatment technologies and source-zone bioremediation. The objective of this paper is to review and integrate knowledge gained from recent demonstrations of field-scale source-zone remediation with that from laboratory investigations of solvent biotransformation to assess the potential promise of technology coupling. This work differs from published reviews of specific technologies (e.g., Bradley 2003; Henry et al. 2003) in its focus on the influence of physical-chemical treatment technologies on post-treatment microbial reductive dechlorination. A technology assessment is provided and recommendations for future work are presented. Although some observations may be generally applicable to any DNAPL site, the focus



herein is on sites where source-zone contamination is comprised in large part of chlorinated solvents (e.g., PCE, TCE).

### **Chlorinated Ethene Biodegradation**

The degradation of chlorinated ethenes in microcosms and the detection of degradation products at contaminated groundwater sites in the 1980's inspired researchers to investigate biotic and abiotic transformation processes (McCarty and Semprini 1994; Vogel and McCarty 1985; Vogel et al. 1987). As early as 1980, researchers identified links between microbial metabolism and the destruction of chlorinated hydrocarbons (Higgins et al. 1980). As more work was completed, researchers recognized that oxidation or reduction of chlorinated hydrocarbons under different redox conditions is feasible (Table 1). The following discussion briefly reviews microbial dechlorination processes that can occur in the subsurface and identifies those processes that are most promising for stimulation in a source zone following active mass removal. For a more thorough discussion of chloroethene biodegradation see reviews by Bradley (2003), Holliger (1995), Janssen et al. (2001), Semprini (1997, 2001), or Smidt and de Vos (2004).

Although oxidation of chlorinated hydrocarbons in both aerobic and anaerobic environments has been demonstrated (Bradley et al. 1998; Bradley and Chappelle 1996; Coleman et al. 2002a, 2002b; Hartmans et al. 1985; Hartmans and deBont 1992; Singh et al. 2004; Vercé et al. 2000, 2001), aerobic metabolic oxidation is a productive pathway only for removal of lesser chlorinated ethenes (i.e., *cis*-DCE and VC). No organisms that grow aerobically with PCE or TCE as a carbon source have been identified. In anoxic environments, the metabolic oxidation of chloroethenes is still poorly understood. Although the mineralization of *cis*-DCE and VC under iron- and manganese-reducing condition has been demonstrated (Bradley et al. 1998; Bradley and Chappelle 1996), the relevance of this process for bioremediation has yet to be established. Cometabolism is an alternative non-metabolic process that has been shown to transform contaminants in both aerobic and anaerobic

environments (Anderson and McCarty 1997; Chauhan et al. 1998; Ensign et al. 1992; Hopkins et al. 1993; Ryoo et al. 2001; Shim et al. 2001). Aerobic cometabolism can act on all chloroethenes (Ryoo et al. 2001; Shim et al. 2001), however the need for a primary substrate such as methane or toluene, and the fact that the degradation of the target compounds can only be indirectly controlled, are major drawbacks of this approach. Anaerobic cometabolic reductive dechlorination of PCE has been observed under methanogenic (Fathepure and Boyd 1988a, 1988b), acetogenic (Terzenbach and Blaut 1994), and sulfidogenic conditions (Cole et al. 1995). However, due to low rates and incomplete dechlorination, this process is least likely to contribute to detoxification of contaminated subsurface environments. More recently, chlororespiration, a process in which chlorinated compounds serve as a metabolic electron acceptor for energy generation, has been demonstrated (Holliger et al. 1998; Löffler et al. 1996, 1999; Smidt and de Vos 2004). The metabolic reductive dechlorination pathway (chlororespiration) is a strict anaerobic process that requires an electron donor (i.e., source of reducing equivalents). The chlororespiratory pathway is promising in that it can lead to efficient dechlorination to ethene and achieve complete detoxification (He et al 2003a, 2003b).

The ability to use chloroethenes as energy-yielding electron acceptors is distributed among several bacterial groups including different subdivisions of the proteobacteria, the gram-positive bacteria, and the Chloroflexi (formerly green non-sulfur bacteria). Organisms capable of metabolic reductive dechlorination (i.e., chlororespiration) have been isolated from contaminated and pristine sites (Smidt and de Vos 2004). These populations are generally strict anaerobes, with only *Enterobacter* strain MS-1 exhibiting facultative metabolism (Sharma and McCarty 1996). Bacterial populations capable of gaining energy from reductive dechlorination of chloroethenes have been classified into a number of phylogenetic groups including *Dehalobacter*, *Sulfurospirillum*, *Desulfuromonas*, *Desulfitobacterium*, *Clostridium*, and *Dehalococcoides* (Bradley 2003; Löffler et al. 2003; Smidt and de Vos 2004). This broad range of organisms capable of chlororespiration is encouraging for post-treatment bioremediation; however, the majority of these organisms are incapable

of complete dechlorination of chloroethenes to ethene (Löffler et al. 2003; Major et al. 2003). At many sites, dichloroethenes (primarily *cis*-DCE), and in some cases vinyl chloride (VC), accumulate. Cupples et al. (2004) recently demonstrated dechlorination of *cis*-DCE and VC, but they identified a minimum threshold chlorinated contaminant concentration below which dechlorination could not be sustained. There is an apparent link between the presence of members of the *Dehalococcoides* group and complete dechlorination (i.e., ethene formation) (Cupples et al. 2003; He et al. 2003a, 2003b; Hendrickson et al. 2002; Maymo-Gatell et al. 1997, 2001; Ritalahti et al. 2001). *Dehalococcoides ethenogenes* strain 195 was the first isolate described to dechlorinate PCE to ethene but the last dechlorination step, VC to ethene, was cometabolic and slow (Maymo-Gatell et al. 1997). A major breakthrough was the isolation of *Dehalococcoides* sp. strain BAV1, the first isolate capable of using all dichloroethene isomers and VC as growth-supporting electron acceptors (He et al. 2003a, 2003b).

While it was originally believed biotransformation processes could not occur near a chlorinated solvent source zone due to the toxicity of high contaminant concentrations associated with the presence of NAPL (Abelson 1990; Bouwer 1994; Robertson and Alexander 1996), recent chlororespiration investigations have been performed in the presence of non-aqueous phase PCE (Adamson et al. 2004; Carr et al. 2000; Cope and Hughes 2001; Dennis et al. 2003; Nielsen and Keasling 1999; Sung et al. 2003; Yang and McCarty 2000, 2002). Nielsen and Keasling (1999) demonstrated complete reductive dechlorination (e.g., ethene formation) at saturated PCE concentrations in batch systems with a dechlorinating consortium. The majority of reducing equivalents from the electron donor (glucose) was consumed in reductive dechlorination probably due to the inhibition of other microbial processes by the high chloroethene concentrations. Yang and McCarty (2000) also reported degradation of PCE in batch systems where concentrations of PCE approached the aqueous solubility limit. Although dechlorination stalled at *cis*-DCE, incomplete dechlorination could still be beneficial for source-zone bioremediation because (1) dissolution rates are enhanced three- (Yang and McCarty 2002, 2003) to six-fold (Cope and Hughes 2001), and (2) *cis*-DCE and VC are more accessible to aerobic degradation

in down-gradient aerobic zones (Coleman et al. 2002a, 2002b). In column studies, a nonuniform distribution of NAPL and organisms resulted in significant competition for reducing equivalents and bioclogging due to excessive microbial growth of non-dechlorinating biomass (Yang and McCarty 2002). Competition and bioclogging may be controlled by slow release electron donors. However, application of a simplified numerical model suggested that under electron donor limiting conditions, a biofilm develops around the NAPL, reducing dissolution and increasing the difficulty of supplying sufficient electron donor (Chu et al. 2003). Partitioning of lesser chlorinated ethenes (TCE, *cis*-DCE, VC) into PCE-DNAPL and decreases in pH due to the release of HCl have also been observed, and may impact the dechlorination of the lesser chlorinated ethenes (Adamson et al. 2004; Cope and Hughes 2001).

These findings have important ramifications for source-zone bioremediation, as well as post-treatment biopolishing. Although a variety of organisms are capable of PCE-to-*cis*-DCE dechlorination, complete detoxification requires the presence and activity of *Dehalococcoides* populations (Ritalahti et al. 2001; Hendrickson et al. 2002). Contaminant removal and plume containment following bioaugmentation with *Dehalococcoides*-containing cultures has been demonstrated in the field (Ellis et al. 2000; Lendvay et al. 2003; Major et al. 2002), and recent results suggest that bioaugmentation is also a viable approach for initiation of reductive dechlorination in PCE source zones (Adamson et al. 2003). These findings suggest that combined bioaugmentation strategies that (i) initiate the reductive dechlorination process in source zones (Adamson et al. 2003) following physical-chemical treatment, and (ii) establish bioreactive barriers for treatment of dissolved contaminants down-gradient (Lendvay et al. 2003) are promising remediation approaches that warrant further exploration.

To sustain the reductive dechlorination process, a source of reducing equivalents (i.e., an electron donor) must be provided. Chlororespiring populations depend on the activity of fermentative organisms to convert (complex) organic materials into suitable electron donors (e.g., hydrogen or

acetate) (DiStefano et al. 1992; He et al. 2002). A variety of substrates including pentanol, ethanol, lactate, propionate, butyrate, and oleate have been shown to produce suitable electron donors (e.g., acetate, hydrogen) to support chlororespiring populations (Carr and Hughes 1998; Fennell and Gossett, 1998; He et al. 2002; Yang and McCarty 1998, 2002). Alternative amendment strategies that supply slow-release, non-soluble substrates (e.g., olive oil, chitin, polylactate esters [e.g., HRC]) have also been successfully used (Koenigsberg and Farone 1999; Yang and MacCarty 2002). Chlororespiring populations are highly competitive hydrogen utilizers, and outcompete methanogens, acetogens, and sulfate-reducing populations for this electron donor (Löffler et al. 1999). Thus, substrates that result in slow release (or production) of hydrogen are advantageous because the majority of reducing equivalents is directed towards the process of interest (Ballapragada et al. 1997; Fennell et al. 1997; Fennell and Gossett 1998; He et al. 2002; Smatlak et al. 1996). It should be noted that any approach that increases the flux of hydrogen in a subsurface environment will also result in an increased flux of acetate, which has been implicated as a relevant source of low concentrations of hydrogen through syntrophic oxidation (He et al. 2002; Schink 1997).

### **Physical-Chemical Treatment of Chlorinated Solvent Source Zones**

Over the past decade, a number of innovative technologies have been developed that show promise for recovering a large fraction of the DNAPL mass at a given site (e.g., Brusseau et al. 1999; Stroo et al. 2003). Although the number of field-scale demonstrations of these technologies is growing, more standardization of assessment and reporting of results are necessary before larger-scale implementations can be considered sound practice (NRC 1997). Furthermore, the lack of consensus pertaining to the potential benefits of partial source-zone removal (e.g., Rao et al. 2002; Rao and Jawitz 2003; Sale and McWhorter 2001) points to the need for a better understanding of the long-term influence of physical-chemical treatment on contaminant fluxes, plume development, and enhanced microbial activity.

Given that innovative source-zone removal technologies have been extensively documented (e.g., NRC 1994, 1997, 1999), this paper will offer only a brief summary of selected approaches including air sparging, chemical oxidation, thermal treatment, co-solvent flushing, and surfactant-enhanced aquifer remediation. Application of any of these treatment technologies would require detailed site characterization, a well-delineated source-zone, and in most cases, efficient contact between injected fluids and DNAPL. The discussion below focuses on assessing the potential for coupling each technology with microbial reductive dechlorination.

*Air Sparging.* A source-zone remediation technology that has been implemented at many DNAPL contaminated sites is air sparging (NRC 1997, see Brown 1997; Hinchee 1994; Johnson et al. 1993; Reddy et al. 1995; Suthersan 1996 for more detailed descriptions and reviews of air sparging technologies). Air is injected below the water table to volatilize or strip contaminants from groundwater (see Figure 2). The vapor-phase contaminant rises into the unsaturated zone where it can then be extracted with a soil vapor extraction system (Johnson et al. 1993). Typically, design of these systems is empirical and based upon two primary assumptions: (1) the gas phase will contact the non-aqueous phase, resulting in direct mass transfer from the DNAPL to the vapor phase, and (2) the gas phase will strip dissolved contaminants from the aqueous phase (Suthersan 1997; Unger et al. 1995).

While air sparging may be applied to reduce DNAPL mass (Unger et al. 1995), concerns remain that the introduction of air to a source zone may increase the extent of contamination through lateral and vertical spreading of NAPL (Blanford et al. 1999; Henry et al. 2003). Air sparging has been reported to stimulate aerobic microbial processes including cometabolism of chlorinated ethenes as long as a suitable primary substrate is present (Gierke et al. 1999; Johnson et al. 1993; Raes et al. 2002). Sustained enhanced aerobic biodegradation however, may be problematic as aerobic degradation of unsaturated chlorinated solvents is limited at the high contaminant concentrations commonly found within DNAPL source zones (Alvarez-Cohen and McCarty 1991). The

implementation of the aerobic cometabolic process has been successfully demonstrated for TCE removal under field conditions (McCarty et al. 1998), however the requirement for a primary substrate (e.g., toluene) remains problematic. Although lower chlorinated ethenes (e.g., *cis*-DCE and VC) are amenable to growth-linked microbial degradation under aerobic conditions, a metabolic process capable of oxidizing PCE and TCE has yet to be identified (Löffler et al. 2003). For these reasons it is unlikely that stimulation of reductive dechlorination following air sparging is a viable approach.

*Chemical Oxidation.* In situ chemical oxidation (ISCO) was developed to transform contaminants into benign products (i.e., CO<sub>2</sub> and salts) (see NRC 1999 and Siegrist et al. 2001 for mechanistic descriptions of ISCO technologies). A common form of this technology involves the injection of hydrogen peroxide (~10% to 50% by weight) in conjunction with an iron catalyst (e.g., ferrous sulfate), which forms highly reactive hydroxyl radicals (OH•) via Fenton's chemistry. The hydroxyl radicals are strong oxidants and react rapidly with surrounding molecules. Solutions of hydrogen peroxide, without catalyst, have been introduced into the subsurface (Oberle and Schroder 2000) to reduce iron catalyst requirements and the need for pH adjustments. However, hydrogen peroxide at ambient temperature and pressure is a relatively poor oxidizing agent for chlorinated solvents. When hydrogen peroxide solutions are injected alone (i.e., without an iron catalyst) reductions in contaminant concentrations are frequently the result of volatilization or stripping, which occurs due to increased temperature and O<sub>2</sub> production as the hydrogen peroxide decomposes (Oberle and Schroder 2000). Permanganate, in the form of either NaMnO<sub>4</sub> or KMnO<sub>4</sub>, offers an attractive alternative to Fenton's chemistry as it does not rely on the formation and transport of short-lived OH• radicals. The use of permanganate, however, results in the formation of MnO<sub>2</sub>, which may precipitate and reduce aquifer permeability (Dai and Reitsma 2002; Li and Schwartz 2003; Siegrist et al. 2001). The potential for permeability reduction, as well as increased metal mobility, that may accompany use of chemical oxidants, depends upon site specific geochemical conditions. Thus, as with all source-zone treatment

technologies, thorough site characterization is required to mitigate potential adverse effects (Crimi and Siegrist 2003; Siegrist et al. 2001).

Application of chemical oxidation to DNAPL source zones (Figure 3) has produced mixed results (Siegrist et al. 2001; Urynowicz and Siegrist 2000). Still, some evidence suggests permanganate oxidation of DNAPLs may be plausible if delivery of chemical oxidants to DNAPL mass can be improved (Nelson et al. 2001; Schnarr et al. 1998; West et al. 1998), and MnO<sub>2</sub> crusting of the DNAPL avoided (Dia and Reitsma 2002; Li and Schwartz 2003; Siegrist et al. 2001). These issues notwithstanding, the fate of microorganisms through the oxidation process remains unclear (Bassel and Nelson 2000; Kastner et al. 2000). While a limited number of studies indicate both aerobic and anaerobic populations may rebound following treatment with relatively low concentrations (<2% wt) of oxidants (e.g., Allen and Reardon 2000), the post-treatment environment may have pH levels that are unfavorable for microbial activity depending upon site conditions (Kastner et al. 2000, Siegrist et al. 2001). Additionally, permanganate residuals in the source zone, or oxygen produced during treatment is likely to maintain oxidative conditions, which prohibit reductive dechlorination of chloroethenes.

*Thermal Treatment.* Thermal treatment techniques include steam (or hot water) flooding, resistive heating (e.g., three- or six-phase heating), conductive heating (e.g., thermal blankets), or some combination thereof (more detailed descriptions of several thermal technologies may be found in Falta 2000; NRC 1999; Udell 1997). Of these technologies, steam flushing is frequently employed for treatment of sites contaminated with NAPL (see Figure 4). Laboratory and field tests have demonstrated the robustness of steam flushing (Udell 1997). There are, however, two drawbacks limiting widespread implementation: 1) energy demands contribute significantly to project costs (Henry et al. 2003) and 2) the potential for NAPL mobilization (Davis and Heron 1998; Falta 2000). During steam flushing, DNAPL mobilization occurs through a reduction in capillary forces at the



condensation front, and may become problematic if the recondensed organic liquid phase escapes hydraulic control and contaminates pristine regions of the subsurface. Thus, recent work focused on designs that reduce the potential for downward migration of DNAPLs during steam flooding (Kaslusky and Udell 2002). Lesser understood impacts of steam treatment include the potential formation of intermediates or byproducts during thermal degradation (Cai and Guengerich 1999; Davis and Heron 1998; Kline et al. 1978; McKinney et al. 1955), and effects of steam and high temperatures on the microbial community (Davis 1998; Richardson et al. 2002).

Long-term monitoring efforts provide limited evidence that microbial activity may rebound following field-scale steam treatment (Smith et al. 1998, 2000). Richardson et al. (2002) found that mesophilic bacterial and archaeal populations survived steam treatment in laboratory studies using soils collected from contaminated sites. In their study microbial activity was only detectable after periods of gradual cooling; elevated temperatures and fast cooling rates resulted in little or no microbial activity. In situ rates of cooling are anticipated to be slow enough to allow subsequent microbial rebound (Richardson et al. 2002). Thorough characterization of the subsurface environment following thermal treatment of DNAPL source zones has yet to be reported, but it is likely that the treated zone immediately following steam or hot water injection will be aerobic, given that air may be injected during treatment for the purposes of contaminant oxidation (Leif et al. 1998) or DNAPL mobility control (Kaslusky and Udell 2002). In contrast, redox potentials measured at a site following electrical resistive heating were found to be consistent with those required for reductive dechlorination (Beyke et al. 2000; Smith et al. 2000). Therefore, additional research is required to determine the effectiveness of employing microbial reductive dechlorination following thermal treatment of DNAPL source zones.

*Co-Solvent Flushing.* Alcohols have been utilized as co-solvents to enhance recovery of NAPLs through either solubilization or mobilization (displacement) (Figure 4, see AATDF 1997; Augustijn et

al. 1997; Falta 1998 for description of the mechanisms and implementation of co-solvent flushing technologies). During solubilization, NAPL remains relatively immobile throughout recovery. In contrast, mobilization relies upon reduced capillary forces resulting from a decrease in interfacial tension to facilitate release and displacement of NAPL ganglia, which are recovered as an organic liquid or free product. While mobilization and solubilization are not mutually exclusive processes, co-solvent floods may be designed to favor either mechanism through a detailed understanding of system phase behavior (Brandes and Farley 1993; Falta 1998). Although selection of alcohols to promote partitioning leading to reductions in the density difference between phases (e.g., Lunn and Kueper 1999) can mitigate downward migration of DNAPL, field implementation of mobilization co-solvent floods have been limited to the treatment of LNAPL source zones (Falta et al. 1999). Other field tests employing the use of co-solvents focused on enhanced removal through solubilization (Rao et al. 1997; Jawitz et al. 2000). Use of high concentrations of alcohols (>70%) in co-solvent flushing may result in gravity override (bypassing) and reduced source-zone bioactivity. Gravity override can be limited with careful design of injection systems to counter buoyancy forces (Jawitz et al. 2000). Although flushing with concentrated alcohol solutions may negatively impact microbial activity, long-term monitoring results (>3 years) from a site where co-solvent flushing was employed suggest that general bioactivity may rebound as alcohol concentrations decrease (Annable 2003; Mravik et al. 2003). It is unclear, however, how the populations critical to reductive dechlorination respond to alcohol flushing. In general, if harmful impacts on the microbial community can be avoided, or are shown to be less disruptive than currently perceived, the addition of short chain alcohols such as ethanol may prove to be a feasible method for stimulating post-treatment reductive dechlorination.

*Surfactant-Enhanced Aquifer Remediation.* Surfactant enhanced aquifer remediation (SEAR) refers to in situ flushing technologies that utilize surfactants to overcome many of the limitations experienced during pump-and-treat remediation of DNAPL source-zones (Figure 4, mechanistic and practicable

descriptions of SEAR include: AATDF 1997; Jafvert 1996; Pennell and Abriola 1997). Generally, surfactants are molecules that preferentially accumulate at surfaces or interfaces based upon their amphiphilic molecular structure. Both anionic and non-ionic surfactants have demonstrated potential for use in NAPL-contaminated aquifer remediation (Baran et al. 1994; Dwarakanath et al. 1999; Pennell et al. 1993; Shiau et al. 1994). SEAR technologies are similar to co-solvent flushing in that the general mechanisms of source-zone mass removal are solubilization and mobilization (Figure 4 inset). As is the case with most aggressive remediation approaches, SEAR leverages greater upfront capital expenditures than traditional pump-and-treat remediation for higher efficiency. Upwards of 90% recovery of contaminant mass has been demonstrated within DNAPL source zones in short time periods at the field scale (Abriola et al. 2002; Londergan et al. 2001; Ramsburg et al. submitted-a). The efficiency of SEAR makes it an attractive alternative to pump-and-treat remediation where hydraulic control allows for near complete capture of injected surfactant. One drawback to the use of surfactant solutions designed for high contaminant solubilization is the possibility of downward migration of the relatively dense solubilized plume or mobilized free-product DNAPL prior to recovery. Plume plunging behavior, however, may be mitigated through the addition of alcohols to the surfactant solution (Kostarelos et al. 1998) and careful design of the hydraulic flow regime/control system (Abriola et al. 2002; Abriola et al. submitted). Concerns over downward migration of mobilized DNAPL may be alleviated by utilizing SEAR technologies that reduce DNAPL density in situ prior to mobilization (Ramsburg et al. 2003; Ramsburg and Pennell 2002; Yan et al. 2003)

Use of readily biodegradable, food-grade surfactants minimizes concerns over the fate of unrecovered surfactant, yet the effect of such surfactants on microbial populations responsible for reductive dechlorination within the swept zone is only now beginning to be explored. While most anionic and nonionic surfactants considered for application are completely degradable under aerobic conditions (Swisher 1987), degradation of alkylphenol ethoxylates (e.g., Triton X-100) has been shown to generate products (e.g., alkylphenols) which are persistent, toxic and estrogenic (e.g., Ahel et al.

1994a, 1994b; Stephanou and Geiger 1982; White et al. 1994). Residual levels of readily degradable, food-grade surfactants, however, will likely promote the establishment of anaerobiosis, potentially facilitating conditions conducive for reductive dechlorination.

Application of biodegradable anionic surfactants at field sites has typically been accompanied by high concentrations of 2-propanol (~40 g/L) and sodium chloride (as high as 7 g/L) to increase contaminant solubilization capacities upwards of 60 g/L (e.g., Brown et al. 1999). Thus, post-treatment conditions will likely have elevated concentrations of anionic surfactant, alcohol and sodium chloride, which could inhibit or prevent microbial activity. Unfortunately, no long-term monitoring results have been reported, limiting our understanding of microbial activity following treatment with these formulations. In contrast, long term monitoring results from a field test conducted using a biodegradable, food-grade, nonionic surfactant (without alcohol or salt addition) indicate that surfactant degradation stimulated microbial activity within the treated source zone (Abriola et al. 2003; Ramsburg et al. submitted-b).

#### *Implications for Coupling Physical-Chemical Treatment with Microbial Reductive Dechlorination.*

Existing evidence suggests certain physical-chemical source-zone treatment technologies are more promising for the stimulation of microbial activity as a post-treatment polishing step. While air sparging, chemical oxidation, and steam flooding may generate an aerobic environment suitable for subsequent metabolic or co-metabolic oxidation, SEAR and co-solvent flushing appear to be the most promising physical-chemical treatments for integration with the microbial reductive dechlorination process. Note that in this assessment the possibility that DNAPL contaminant distributions resulting from aggressive treatment may be technology specific has not been considered due to the scarcity of data. Residual alcohol or surfactant solutions contribute to oxygen depletion and establishment of anaerobic conditions following aggressive treatment. Further, residual flushing solution may serve as a source of reducing equivalents, and stimulate the reductive dechlorination process. Although other

technologies may eventually be successfully integrated with post-treatment microbial reductive dechlorination, SEAR seems particularly applicable due to limited toxicity on the microbial community, the establishment of reducing conditions, and the release of reducing equivalents for stimulation of the reductive dechlorination process. Thus, the ultimate fate of the residual surfactant solution and its effect on the dechlorinating population must be considered.

While microbial degradation of surfactants in aerobic environments is well documented (Swisher 1987), it is uncertain how surfactants typically selected for SEAR are degraded in anaerobic environments. Linear alcohol ethoxylates are degraded to fermentable substrates under anaerobic conditions (Huber et al. 2000), and the degradation of nonionic surfactant has been reported under methanogenic conditions (Yeh et al. 1999). It is, therefore, likely that fermentation of unrecovered surfactant will serve as an indirect source of reducing equivalents by producing hydrogen and organic acids, whose slow anaerobic oxidation will generate additional hydrogen to support the chlororespiring populations.

The residual surfactant concentrations, however, may also alter the bioavailability of a contaminant (Colores et al. 2000; Pennell et al. 2001; Rouse et al. 1994). Yeh et al. (1999) investigated the bioavailability of hexachlorobenzene (HCB) in the presence of nonionic, ethoxylated sorbitan surfactants (i.e., Tween series) in a methanogenic mixed culture obtained from contaminated sediment. At low surfactant concentrations (<10 mg/L) there was no apparent change in rate or extent of HCB dechlorination. At a surfactant concentrations above the critical micelle concentration (CMC) enhanced HCB dissolution occurred, and although dechlorination rates decreased, the dechlorination endpoint remained unchanged. Complete inhibition of reductive dechlorination was observed at a surfactant concentration of 1,000 mg/L. However, Yeh et al. (1999) hypothesized that the observed inhibition was likely due to toxic effects of high surfactant concentrations rather than micellar sequestration of HCB. These results are supported by a recent study using a PCE dechlorinating consortium and a matrix of anionic, nonionic, and cationic surfactants (McGuire and Hughes 2003).

McGuire and Hughes (2003) observed that the nonionic surfactant Tween 80 (polyoxyethylene (20) sorbitan monooleate) exhibited the least impact on dechlorination (both rate and extent), and thus speculated that the number of ethylene oxide groups present on the surfactant molecule impacts surfactant toxicity. In fact, Bury and Miller (1993) and Guha et al. (1998) demonstrated that contaminants (in these studies nonchlorinated hydrocarbons) sequestered in the micellar phase may remain bioavailable. The response of the dechlorinating microbial community to surfactants is poorly understood, and future research should explore possible stimulatory or inhibitory effects in a heterogeneous environment where local surfactant concentrations may be well above the CMC.

### **Mathematical Assessment**

Although biological reduction of PCE in DNAPL source zones may be feasible, the relatively low dissolution enhancement factors (three- to six-fold) reported imply that source longevity would still be measured in multiple decades. Alternatively, if uncertainties in the source zone microbial environment following physical-chemical treatment can be overcome, multiple order-of-magnitude reductions in source-zone mass removal obtained via active physical-chemical treatment might be combined with post-treatment biopolishing to substantially reduce source longevity. Ultimately, it may be possible to devise a post-treatment source-zone strategy that minimizes operations and maintenance efforts while still meeting regulatory standards at down-gradient points of compliance.

The potential benefits of tailoring physical-chemical treatments to stimulate microbial reductive dechlorination may be illustrated through a straightforward mathematical modeling analysis that compares source longevity for four hypothetical DNAPL source-zone scenarios (Figure 5) under three management strategies: (1) natural gradient dissolution (natural dissolution), (2) enhanced reductive dechlorination (source-zone bioremediation), and (3) physical-chemical treatment followed by source-zone biopolishing (SEAR + enhanced reductive dechlorination). The four hypothetical field scenarios were selected to span the range of behavior that may be expected in the field and are characterized by a

ganglia-to-pool (GTP) ratio, which is a measure of the distribution of mass between low saturation ganglia regions and high saturation pool regions in the source zone. The formation properties, spill scenario, and SEAR characteristics were taken from a recent numerical modeling study that was based on a pilot-scale SEAR demonstration at the Bachman Road site in Oscoda, MI (Abriola et al. submitted; Lemke and Abriola 2003; Lemke et al. 2004). These properties are summarized in Table 2. Scenario 1 assumes NAPL is entrapped as residual globules and ganglia at a uniform saturation throughout the source zone (Figure 5a). This scenario has an infinite ganglia-to-pool ratio (IGP) and would be characteristic of an ideal site that had perfectly uniform hydraulic properties and where DNAPL was released over a reasonably wide area. Cleanup of this site is modeled using a simplified hydraulic approach (Brusseau 1996), which is based on mass-balance calculations. Scenario 2 is perhaps more realistic. It is representative of a situation with the NAPL entrapped as residual ganglia (Figure 5b), though some pooling has occurred due to permeability contrasts (high ganglia-to-pool ratio (HGP), GTP greater than 1.0). This DNAPL saturation distribution was generated following the methods outlined by Lemke and Abriola (2003) and Lemke et al. (2004). Using this methodology, the release of NAPL into a nonuniform permeability field is simulated using an laboratory-validated numerical multiphase simulator – MVALOR (Dekker and Abriola 2000; Lemke et al. 2003; Rathfelder et al. 2001). Natural dissolution or surfactant enhanced aquifer remediation is then simulated using a separate numerical simulator (MISER) that has been used to accurately simulate SEAR in laboratory experiments (Rathfelder et al. 2000, 2001), and was used in the design of a recent SEAR pilot-scale test (Abriola et al., 2002, submitted). Scenario 3 was also generated using this same methodology (Figure 5c). Here, however, formation properties were configured so that the resultant saturation distribution was dominated by pools (low ganglia-to-pool ratio (LGP), GTP less than 1.0) (see Lemke et al. (2004) for details). Scenario 4 assumes all mass is immobilized in six idealized, rectangular, fully saturated ( $S_n = 1$ ) pools with no ganglia remaining (Figure 5d). This scenario is an extreme case where the ganglia-to-pool ratio is equal to zero (ZGP). Cleanup in this scenario was modeled using an

analytical solution to the 2D advection-dispersion equation following the methods of Johnson and Pankow (1992). It should be noted that, in contrast to the HGP and LGP scenarios (1 and 4), which result from the utilization of numerical models that incorporate more of the physics of the problem (e.g., hysteretic DNAPL migration, nonuniform flow, rate-limited dissolution) the IGP and ZGP scenarios are non-physical, idealized end-members intended to bracket behavior that may be observed in the field. Although the distribution of mass in the source-zone is different in each of the four scenarios, the amounts of mass in the source zone, the source-zone (i.e., domain) volume, the aqueous-phase contaminant solubility during a given process (i.e., SEAR or natural gradient dissolution), and the average hydraulic flux through the source zone are identical.

The source longevity in Scenarios 1-4 using each of the three remediation strategies was arbitrarily defined as the time when 99.9% NAPL was removed from the source zone. The second and third management strategies, source-zone bioremediation and SEAR + biopolishing, used a simplified bioenhancement factor taken from the literature to quantify the improvement in dissolution due to microbially mediated aqueous-phase degradation. Reductive dechlorination enhanced-dissolution factors ranging from three- to six-fold have been reported (Cope and Hughes 2001; Yang and McCarty 2002). For this simplified example an enhancement factor of five was assumed. This enhancement factor was reported in column studies in which NAPL ganglia were uniformly distributed, chlororespirers were present and active, and there were no limitations on microbial growth (Yang and McCarty 2000; Cope and Hughes 2001). It is unlikely that these conditions could be obtained at real sites and thus, the enhancement factor of five is likely optimistic. However, in an effort to determine the benefits of aggressive mass removal prior to source-zone biopolishing (management strategy 3) versus bioremediation alone, favorable source-zone bioremediation (management strategy 2) was assumed.

Calculated values of source longevity for each of the three management strategies for all 4 scenarios are reported in Table 3, and percent mass removal as a function of time is presented in Figure



6. As might be expected, source longevity for Scenario 1 (IGP) and Scenario 4 (ZGP) tend to bracket the cleanup behavior of the more complex scenarios (HGP & LGP). Application of physical-chemical source-zone treatment (a 10-day surfactant flush of 4% Tween 80) prior to biopolishing is shown to reduce the source longevity regardless of scenario conditions. The magnitude of this reduction, however, depends on the level of pooling in the NAPL source zone (Figure 6a). If, for example, the LGP scenario is assumed to be representative of a typical small-scale site, the 10-day SEAR followed by biopolishing will result in a 53% and 91% decrease in source longevity, in comparison with results of source-zone reductive dechlorination alone and natural dissolution conditions, respectively (Figure 6b). In this scenario, conducting SEAR operations for an additional 15 days (25 days total) would result in removal of 98.5% of the DNAPL mass thereby reducing source longevity to four years. Thus, results presented in Table 3 and Figure 6 suggest that physical-chemical treatment followed by enhanced microbial activity could greatly reduce source longevity and associated long-term risk.

### **Bachman and Sages**

The co-solvent flood at the former Sages dry cleaning facility (Jacksonville, FL) and the Bachman Road SEAR site (Oscoda, MI) serve as documented case studies where field evidence supports the conclusion that physical-chemical source-zone removal may be coupled with reductive dechlorination. A comparison between observations at the Sages and Bachman sites is shown in Table 4. It is important to recognize that these post-treatment monitoring data provide only a snapshot of conditions (at 1280 day for Sages and 450 day for Bachman) in a transient environment. While the evolutions of the conditions at the Sages and Bachman sites are described in more detail in Mravik et al. (2003) and Ramsburg et al. submitted-b, respectively, the summary herein, facilitates analysis of the observed stimulation of microbial reductive dechlorination following physical-chemical treatment.

At the Sages site, 34,000 L of a solution consisting of 95% (vol) ethanol and 5% (vol) water were flushed through a DNAPL source zone over a period of 3.5 days followed by a 4.5 day water

flood used to recover injected fluids (Jawitz et al. 2000). This co-solvent flood was successful in removing 43 L of PCE-DNAPL from the subsurface, and extraction well data indicate 92% of the ethanol introduced during the flush was recovered (Jawitz et al. 2000). Post-treatment characterization conducted approximately one month following the cessation of flushing activities indicated that DNAPL remained following treatment (Sillan 1999) and that the average PCE and ethanol concentrations in the extraction wells were  $\sim 120 \mu\text{M}$  and  $\sim 230 \text{ mM}$ , respectively (Mravik et al. 2003). Results from longer term sampling at the Sages site indicate that PCE concentrations within the source-zone rebounded to pre-treatment levels approximately 150 days after treatment and that ethanol concentrations remained in excess of 160 mM for approximately 350 days (Mravik et al. 2003). Although ethanol toxicity remains a concern, elevated concentrations of hydrogen and acetate within the treated zone suggest microbial activity (Mravik et al. 2003). Soil samples taken from a core collected down-gradient of the Sages treated zone tested positive when analyzed via nested PCR with *Dehalococcoides*-targeted primers (Mravik et al. 2003). Additionally, microcosm studies with aquifer material from the Sages site indicate sulfate reducing and methanogenic populations rebounded following exposure to elevated concentrations of ethanol (Lindner et al. 2002). While the survival and activity of dechlorinating populations within the treated zone has not been demonstrated to date, observations of significant *cis*-DCE production (up to  $242 \mu\text{M}$ ) at monitoring points located within the treated zone are indicative of microbial reductive dechlorination.

At the Bachman Road site, a pilot-scale field demonstration of SEAR was conducted to remove PCE-DNAPL from beneath a former dry cleaning facility. For this source-zone treatment, 68,400 L of an aqueous solution containing 6% (wt) Tween 80 were introduced over a period of 10 days, with two additional days of active water flooding (Abriola et al. 2002, Abriola et al. submitted; Ramsburg et al. submitted-a). Approximately 95% of the injected surfactant was recovered along with over 19 L of PCE. Post-treatment site monitoring indicate that PCE concentrations were reduced by two orders-of-

magnitude from pre-treatment levels at many locations within the treated zone, and in contrast to the Sages site, did not rebound after 450 days (Abriola et al. 2003; Ramsburg et al. submitted-b). Surfactant concentrations decreased steadily over time, and after 270 days, surfactant was not detectable at most sampling points within the treated zone (12  $\mu$ M detection limit).

Prior to the SEAR treatment, substantial reductive dechlorination had not occurred in the source-zone. However, significant concentrations of PCE degradation products were measured within the treated zone 270 days after treatment (Table 4). Acetate and formate, likely products of Tween 80 fermentation, were observed at levels as high as 4600  $\mu$ M, and are indicative of anaerobic microbial degradation of the surfactant (Abriola et al. 2003, Ramsburg et al. submitted-b). Organic acids are known to support reductively dechlorinating populations present in the Bachman aquifer (He et al. 2002, 2003a, 2003b, Sung et al. 2003), and PCE to *cis*-DCE transformation within the treated source-zone is consistent with laboratory microcosm studies conducted with aquifer material from the Bachman Road site (He et al. 2002). Vinyl chloride, however, was only detected at three out of 26 sampling locations within the source zone. The apparent accumulation of *cis*-DCE at most observation locations may indicate that PCE to *cis*-DCE degrading organisms are predominating within the treated zone.

These two examples from field sites suggest that physical-chemical source-zone treatments are capable of stimulating organisms responsible for degrading residual level contaminants. At these sites, data support the conclusion that ethanol and Tween 80 were metabolized by active microbial communities resulting in an increased production of hydrogen and acetate. The availability of these electron donors, in turn, promoted reductive dechlorination activity. While such enhanced bioactivity within source zones may occur at sites contaminated on much larger scales (e.g., Hill Air Force Base, Londergan et al. 2001), it is important to recognize that sites such as Sages and Bachman are representative of numerous small-scale chloroethene source zones existing in communities across the

United States (e.g., SCRD 2004). These smaller sites are not only significant sources of dissolved phase contamination, they are often more problematic because: 1) they typically occur in proximity to areas of higher population, increasing risk and limiting hydraulic isolation (i.e., containment) options, and 2) the relatively low NAPL saturations and smaller treated volumes at these sites increase treatment costs as quantified by conventional metrics (\$/m<sup>3</sup> of treated soil or \$/L NAPL recovered). Higher costs per volume (treated soil or NAPL) result from a threshold cost associated with establishing a treatment system regardless of site size. Many innovative source-zone technologies offer efficient mass removal at the expense of greater, up-front capital expenditures (Rao et al. 2002). Decreased source longevity resulting from aggressive treatment, however, results in lower operational and maintenance (O&M) costs making many innovative approaches economically viable when compared against long-term pump-and-treat remediation (e.g., Ramsburg and Pennell 2001). A staged treatment approach which employs microbial reductive dechlorination following aggressive mass removal may thus provide a cost-effective option for reduction of both source longevity and risk.

The need for integrating treatment technologies for groundwater cleanup has become more apparent (Jackson 2003; Rao et al. 2002) since first being advocated by the National Research Council (NRC) Committee on Ground Water Clean-up Alternatives (NRC 1994). Thorough site characterization is critical for design of any treatment train remedy (Jackson 2003). Site specific tailoring of physical-chemical treatment for stimulation of post-treatment bioactivity must be based upon an accurate understanding of the location and extent of DNAPL, as well as hydrogeology and pre-treatment microbial parameters. Co-solvent and surfactant flushing are very promising approaches because they can be tailored to enhance post-treatment reductive dechlorination. It should be noted, however, that ISCO may provide another means of polishing of residual-level contamination subsequent to other source-zone remediation technologies. Additionally, ISCO may be an attractive follow-on treatment alternative at sites where characterization efforts demonstrate that dechlorinating populations cannot be readily stimulated or augmented.

## Conclusions

Taken in total, literature data, example calculations, and case studies presented above support a position of cautious optimism regarding the potential of combined physical-chemical/reductive dechlorination remedial methods for the effective treatment of chlorinated solvent source zones. The literature review, however, suggests a number of areas requiring further investigation before the performance of such methods can be fully assessed and optimized. Given the number of remediation sites at which natural attenuation of chlorinated solvents has been documented (Wiedemeier et al. 1999), and the knowledge that many of the flushing solutions themselves stimulate bioactivity in laboratory tests, one would anticipate that stimulation of indigenous microorganisms in a source zone following physical-chemical treatment would be common. Therefore, the lack of widespread evidence for bioremediation following physical-chemical treatment indicates that either microbial activity is occurring but lacks documentation (e.g., the indicators of bioremediation are not monitored) or that the post-treatment environment does not favor microbial activity. It is important that future field demonstrations of source-zone flushing technologies are designed to systematically investigate i) the source-zone (dechlorinating) microbial community, before, during, and following the treatment process, and ii) contaminant and transformation product concentration distributions following treatment. Indeed, to date, most field observations of enhanced reductive dechlorination in treated source zones have been fortuitous, with little thought devoted to microbial processes in the initial design and implementation of the treatment monitoring scheme. Specific culture-dependent (e.g., microcosms) and culture-independent (nucleic acid-based) tools for assessment of the microbial community are now available for this characterization effort (Hendrickson et al. 2002; He et al. 2003a,b; Löffler et al. 2000; Morse et al. 1998).

Future field demonstrations may also be enhanced through exploitation of results obtained from microbial laboratory investigations. Laboratory-scale studies conducted under conditions

representative of a source-zone environment (i.e., in the presence of organic-liquid) provide heuristic, as well as quantitative, guidance for implementation of post-treatment bioremediation. Substrate amendment strategies that favor chlororespiring populations by maintaining a low concentration of hydrogen may be adapted from the laboratory to the field. However, additional work will be required to explore the effect of unrecovered flushing solutions (e.g., alcohol or surfactant) typical of a post-treatment source-zone environment on the metabolism of chlorinated NAPLs by chlororespiring organisms. The discovery of numerous dechlorinating populations capable of converting PCE to *cis*-DCE and recognition of the importance of *Dehalococcoides* populations in the transformation of chloroethenes to ethene will likely improve future bioaugmentation strategies, and further enhance post-treatment biopolishing. Although enhanced NAPL dissolution by partially dechlorinating populations has been demonstrated, it remains to be seen if complete detoxification (e.g., ethene formation) in source zones is feasible.

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**Table 1. Summary of anaerobic and aerobic processes involved in dechlorination/degradation of chlorinated ethenes.**

	Oxidation Processes		Cometabolic Processes		Chlororespiration
	Anaerobic (energy-yielding)	Aerobic (oxygen-dependent) (energy-yielding)	Anaerobic reduction	Aerobic oxidation	
Metabolic group(s)	Fe(III)-reducers Mn(IV)-reducers Humic acid-reducers	<i>Mycobacterium</i> spp. <i>Nocardioides</i> spp. <i>Pseudomonas</i> spp. <i>Polaromonas</i> sp.	Sulfidogens Methanogens Acetogens	Organisms with broad range oxygenases	Anaerobic (energy-yielding reduction)  Chlororespirers
Relative dechlorination/ degradation rates <sup>a</sup>	Unknown	++	+	++ <sup>b</sup>	++++
Frequency of active organisms in nature	Unknown	VC-oxidizers widely distributed in aerobic environments	High in anaerobic environments	High in aerobic environments	Not rare in anaerobic environments
Favorable site conditions	Fe(III) reducing Mn(IV)-reducing	Aerobic	Anaerobic, not e <sup>-</sup> -donor or e <sup>-</sup> - acceptor limited	Aerobic, appropriate substrate present	Anaerobic, appropriate e <sup>-</sup> -donor present, no interfering TEAPs

<sup>a</sup> + = Slow rate, ++ = moderate rate, +++ = fast rate, ++++ = Very fast rate

<sup>b</sup> Dechlorination rates are often not sustained due to accumulation of toxic intermediates

**Table 2. Parameters used in example calculations**

Parameter	Value	Units	Reference
Values used in example calculations			
PCE Spill Volume	0.096	m <sup>3</sup>	Lemke et al. (2004)
Spill radius (r)	0.797	m	Lemke et al. (2004)
Spill depth (h)	8.315	m	Lemke et al. (2004)
Average NAPL Saturation ( $S_o^{AVG}$ )	0.017	-	Lemke et al. (2004)
Porosity (n)	0.36	-	Lemke et al. (2004)
PCE Density ( $\rho_{PCE}$ )	$1.623 \times 10^6$	g/m <sup>3</sup>	Verschueren (1983)
Rate-limited Aqueous-phase PCE concentration ( $C_{aq}^{PCE}$ )	30 <sup>a</sup>	g/m <sup>3</sup>	Abriola et al. (2002, 2003)
Length of surfactant flush	10	d	Abriola et al. (2002, submitted)
Bioenhanced dissolution factor	5 <sup>a</sup>	-	Carr et al. (2000) Cope and Hughes (2001) Yang and McCarty (2002)
Apparent PCE concentration during SEAR (C)	$5.4 \times 10^3$	g/m <sup>3</sup>	Abriola et al. (2002, submitted)
Groundwater Velocity ( $V_d$ )	0.032	m/d	Lemke et al. (2004)
Groundwater Velocity during SEAR	0.514	m/d	Abriola et al. (2002, submitted) Ramsburg et al. (submitted-a)
Pore volume	5.9	m <sup>3</sup>	calculated
Pool length ( $L_p$ )	1	m	calculated
Pool depth	0.016	m	calculated
Number of independent pools	6	-	calculated
Vertical dispersivity ( $\alpha_v$ )	$2.3 \times 10^{-4}$	m	Johnson and Pankow (1992)
Aqueous solubility of PCE	150	g/m <sup>3</sup>	Verschueren (1983)
Equilibrium solubility of PCE in surfactant solution	26,880 <sup>b</sup>	g/m <sup>3</sup>	Taylor et al. (2001)
PCE bulk aqueous phase diffusion coefficient ( $D_{aq}^{PCE}$ )	$5.7 \times 10^{-5}$	m <sup>2</sup> /d	Dekker and Abriola (2000)

<sup>a</sup> Assumed based upon range of reported values

<sup>b</sup> From reported weight solubilization ratio of 0.672 g PCE per g surfactant (4% Tween 80 solution)

**Table 3. Calculated source longevity in years**

Scenario	Natural Gradient Dissolution (yr)	Source-Zone Bioremediation (yr) <sup>a</sup>	SEAR + Biopolishing (yr)
1. Infinite Ganglia-to-Pool ratio (IGP)	36	7	0.01 <sup>b</sup>
2. High Ganglia-to-Pool ratio (HGP)	54	11	0.01 <sup>b</sup>
3. Low Ganglia-to-Pool ratio (LGP)	245	50	24
4. Zero Ganglia-to-Pool ratio (ZGP)	817	163	157

<sup>a</sup> Source-zone bioremediation calculations assume active chlororespiring organisms are present in sufficient numbers and no nutrient or substrate limitations for duration of treatment.

<sup>b</sup> 10-day SEAR (4% Tween) alone was sufficient for 99.9% removal of PCE-DNAPL mass



**Table 4. Comparison of key site parameters and monitoring data**

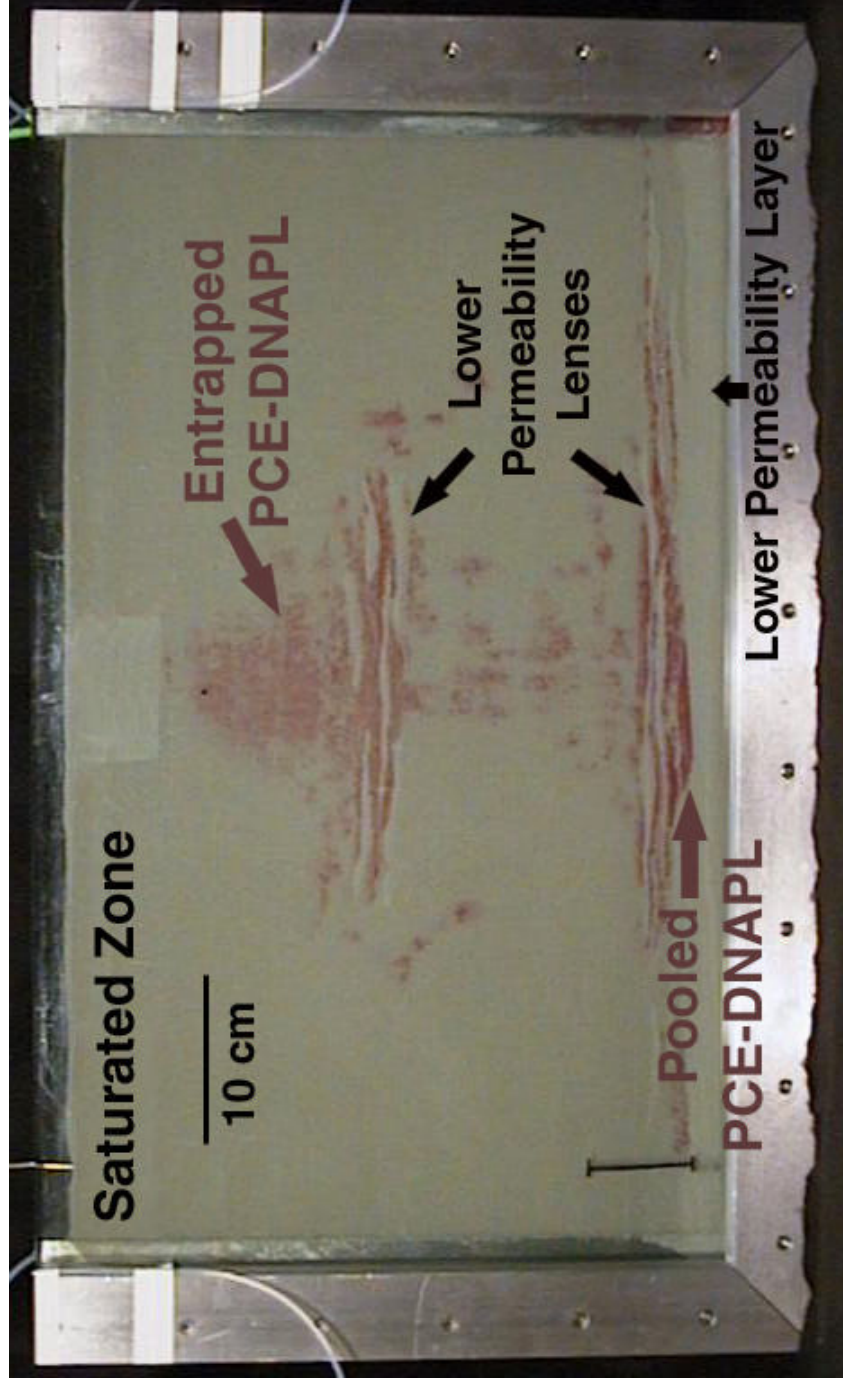
Site	Sages	Ref.	Bachman	Ref.
<b>Site Characteristics</b>				
Location	Jacksonville, FL	(1)	Oscoda, MI	(4)
Former Site Usage	Dry Cleaner	(1)	Dry Cleaner	(4)
Primary Contaminant	PCE	(1)	PCE	(4)
Depth to Groundwater <sup>a</sup>	2.0-2.6 m	(1)	2.4-3.0 m	(4)
Depth to Confining Unit	10 m	(1)	7.6 m	(4)
Range of Hydraulic Conductivity <sup>b</sup>	3-6 m/d	(1)	1-48 m/d	(4)
Soil Classification	Fine Grain Sands	(1)	Medium to Fine Grain Sands	(4)
Areal Extent of Treated Zone	7.3 x 2.7 m	(1)	4.3 x 6.7 m	(4)
Estimated Overall NAPL Saturation	0.004	(1)	0.0004	(5)
Maximum Observed PCE Aqueous Concentration Preceding Treatment	710 µM	(1)	600 µM	(5)
<b>Management Strategy</b>				
Treatment	Co-Solvent	(1)	SEAR	(4)
Flushing Solution	95% (vol) Ethanol	(1)	6% (wt) Tween 80	(5)
Volume of Solution Injected	34 kL	(1)	68 kL	(5)
Duration of Injection	3 day + 4.5 day waterflood	(1)	10 day + 2 day waterflood	(5)
Recovery of Active Ingredient	92% (Ethanol)	(1)	95% (Tween 80)	(5)
PCE Mass Recovery	43 L	(1)	19 L	(5)
Unrecovered Active Ingredient	2000 kg (45 kmol)	(3)	225 kg (0.17 kmol)	(5)
Total Cost	\$440,000	(2)	\$350,000	(5)
<b>Monitoring</b>				
Post-Treatment Monitoring Period	1280 day	(3)	450 day	(6)
Range & (Median) of Concentrations within Treated Zone at Last Reported Monitoring <sup>c</sup>				
PCE	50-150 (100) µM	(3)	0.11-36 (0.38) µM	(6)
TCE	10-30 (20) µM	(3)	0.01-91 (0.09) µM	(6)
cis-DCE	36-242 <sup>d</sup> (150) µM	(3)	0.17-1032 (2.2) µM	(6)
VC	0.07-13 <sup>d</sup> (2.0) µM	(3)	0.02-6.6 (0.02) µM	(6)
Ethene	0.04-0.43 <sup>d</sup> (0.20) µM	(3)	Not Measured	(6)
Acetate	200-600 (400) µM	(3)	100-4600 (100) µM	(6)

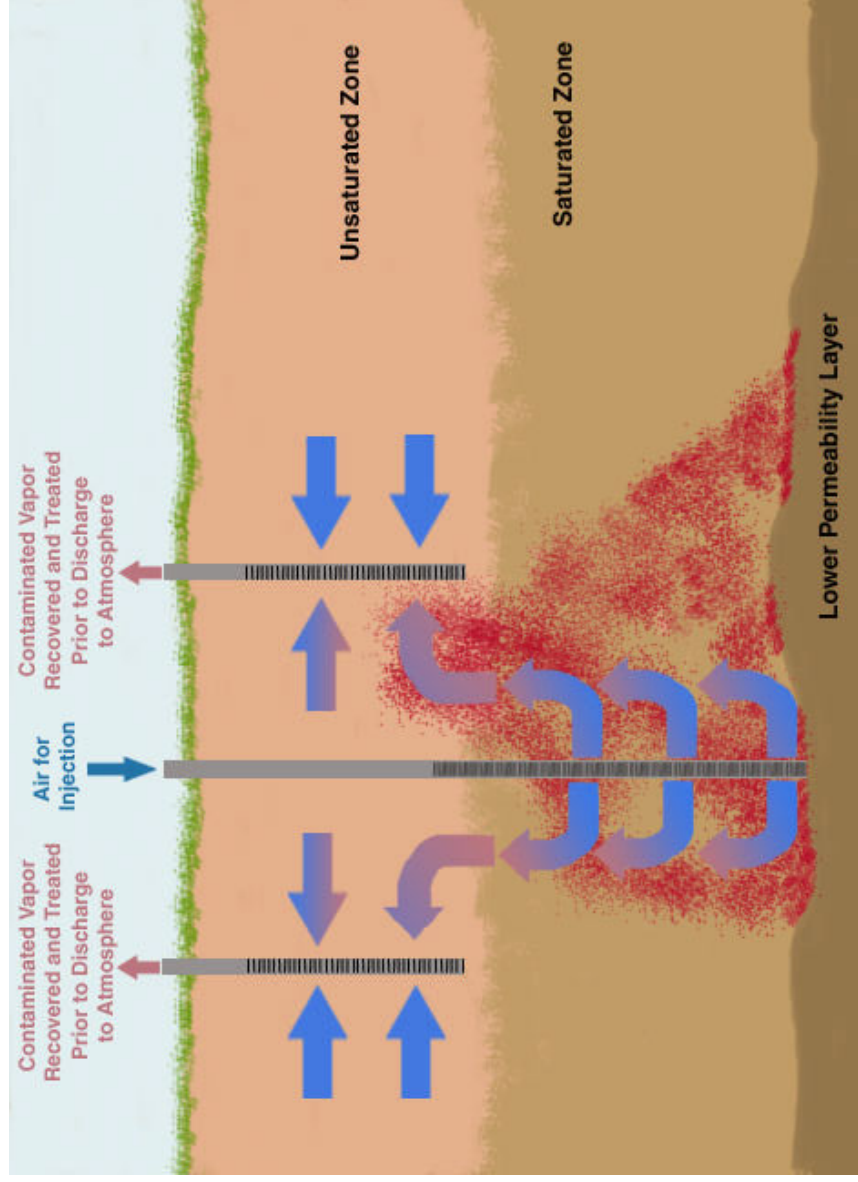
<sup>a</sup> varies seasonally, <sup>b</sup> range due to spatial variability within source zone, <sup>c</sup> values for the Sages site are estimated from kriged contours, <sup>d</sup> actual range (i.e., non-kriged range reported in Mravik et al. 2003)

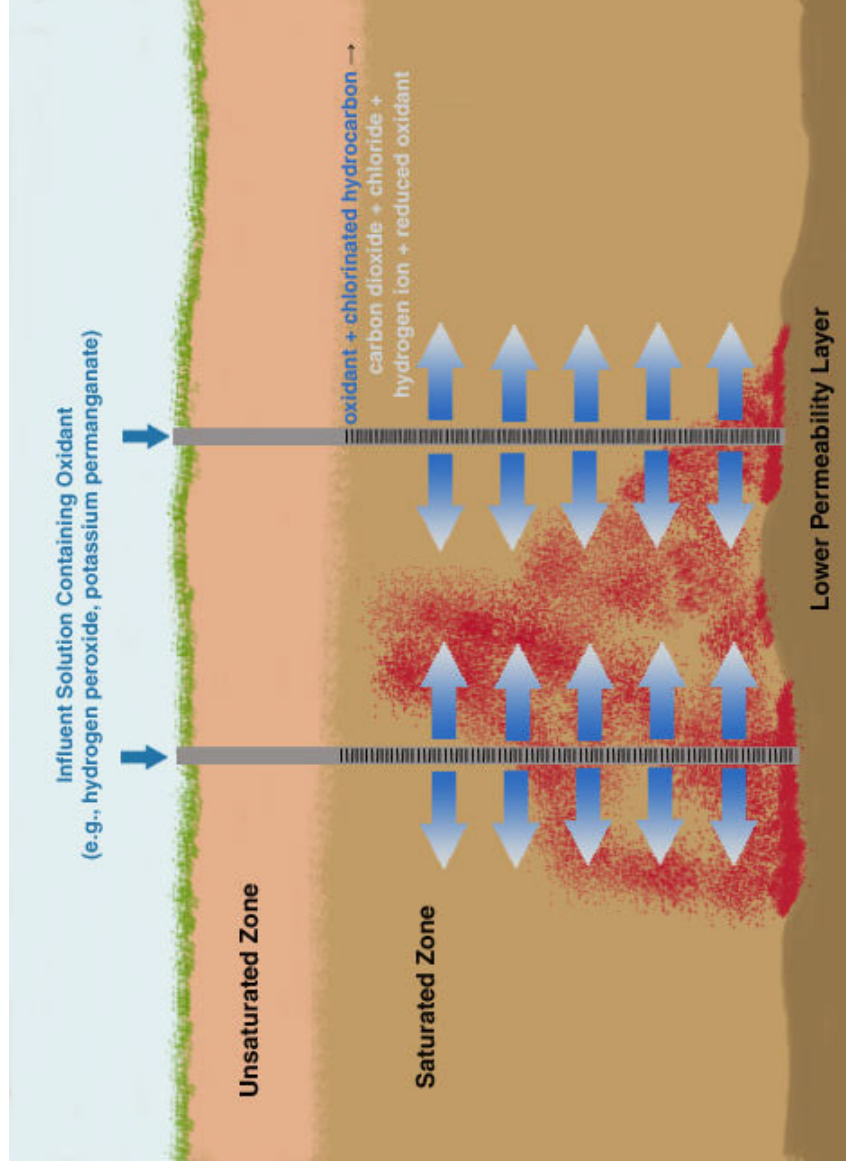
(1) Jawitz et al. 2000, (2) Sillan 1999, (3) Mravik et al. 2003, (4) Abriola et al. submitted, (5) Ramsburg et al. submitted-a, (6) Ramsburg et al. submitted-b

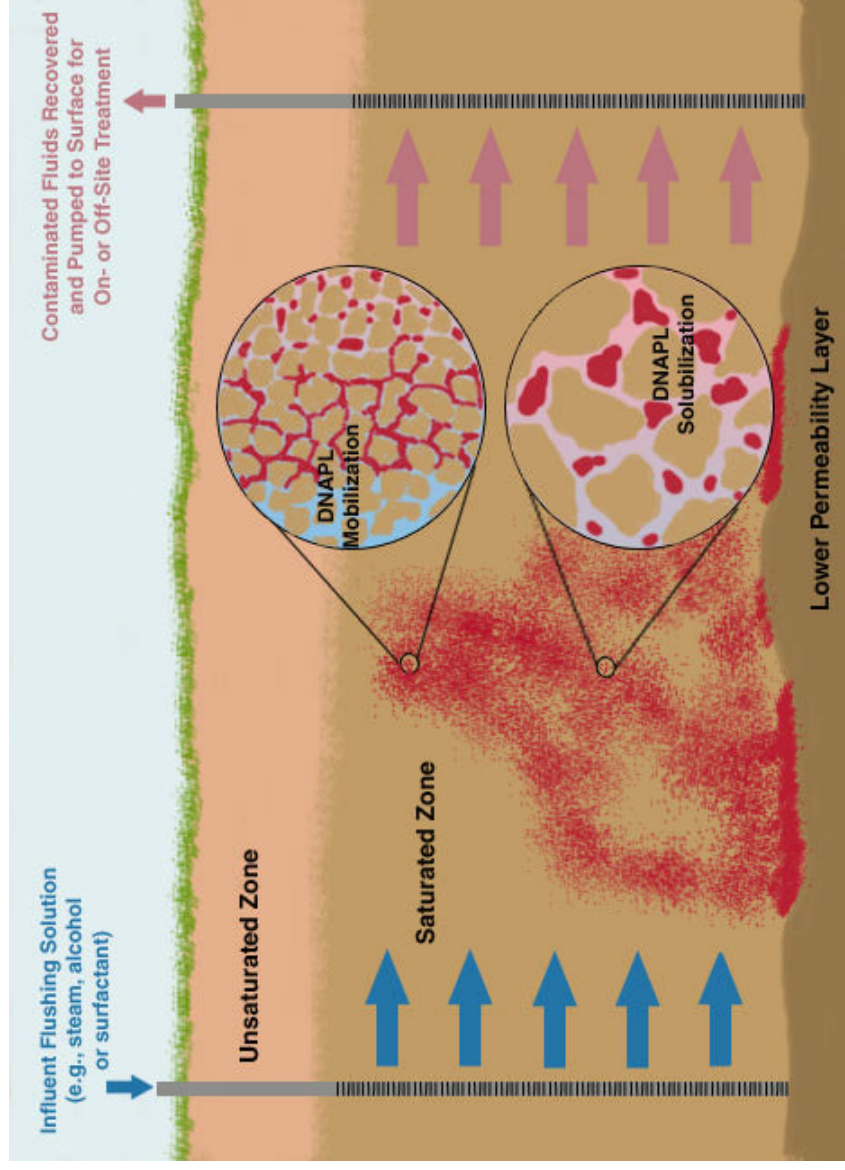
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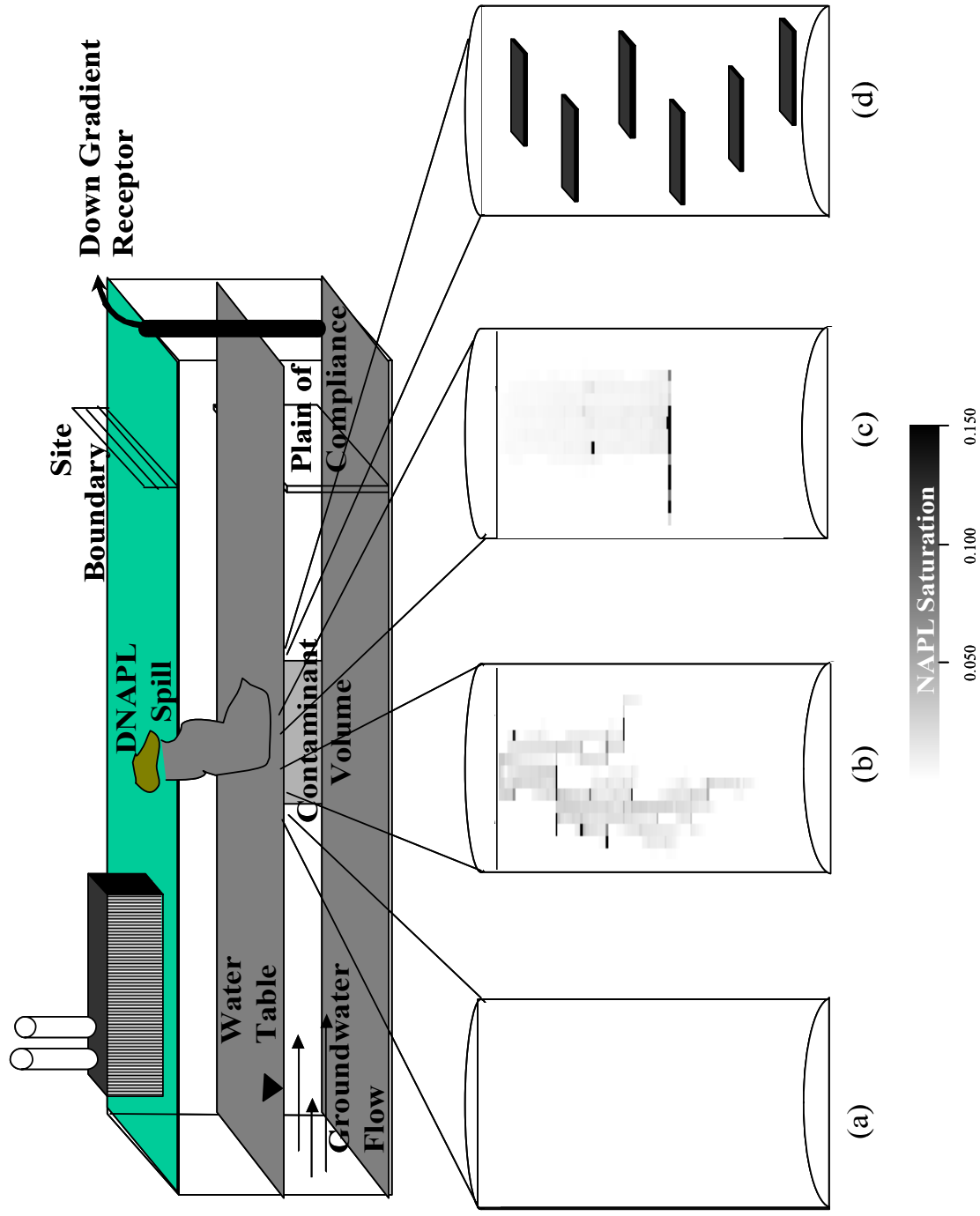
1. Representative photograph from laboratory-scale (63.5 cm length x 38 cm height x 1.4 cm thickness) infiltration and entrapment PCE-DNAPL (dyed red with  $10^{-4}$  M Oil-red-O for visualization).
2. Representation of air sparging with soil vapor extraction in a shallow, relatively homogeneous, unconfined aquifer with a well-defined DNAPL source zone. Arrows represent tortuous air channels into which contaminants partition and are subsequently recovered through soil-vapor extraction wells.
3. Representation of in situ chemical oxidation in a shallow, relatively homogeneous, unconfined aquifer with a well-defined DNAPL source zone. Contaminant destruction occurs in situ as depicted by the representative chemical reaction. Alternatively, implementation of ISCO technologies may utilize a point-to-point flood similar to that shown in Figure 4.
4. Representation of subsurface flushing technologies in a shallow, relatively homogeneous, unconfined aquifer with a well-defined DNAPL source zone (generalized to include steam, co-solvent and surfactant). Insets represent DNAPL recovery mechanisms (top: mobilized bank of free product collecting DNAPL ganglia; bottom: reduction in entrapped DNAPL mass through solubilization).
5. Depiction of DNAPL source-zone conceptual models used in the example calculations: a) infinite ganglia-to-pool ratio (IGP), b) high ganglia-to-pool ratio (HGP), c) low ganglia-to-pool ratio (LGP), and d) zero ganglia-to-pool ratio (ZGP). All control volumes are the same size and contain equal amounts of PCE-DNAPL.
6. Percent of DNAPL mass remaining as a function of time for (a) three alternative remediation strategies in LGP scenario and (b) SEAR followed by bioenhancement in all four scenarios.



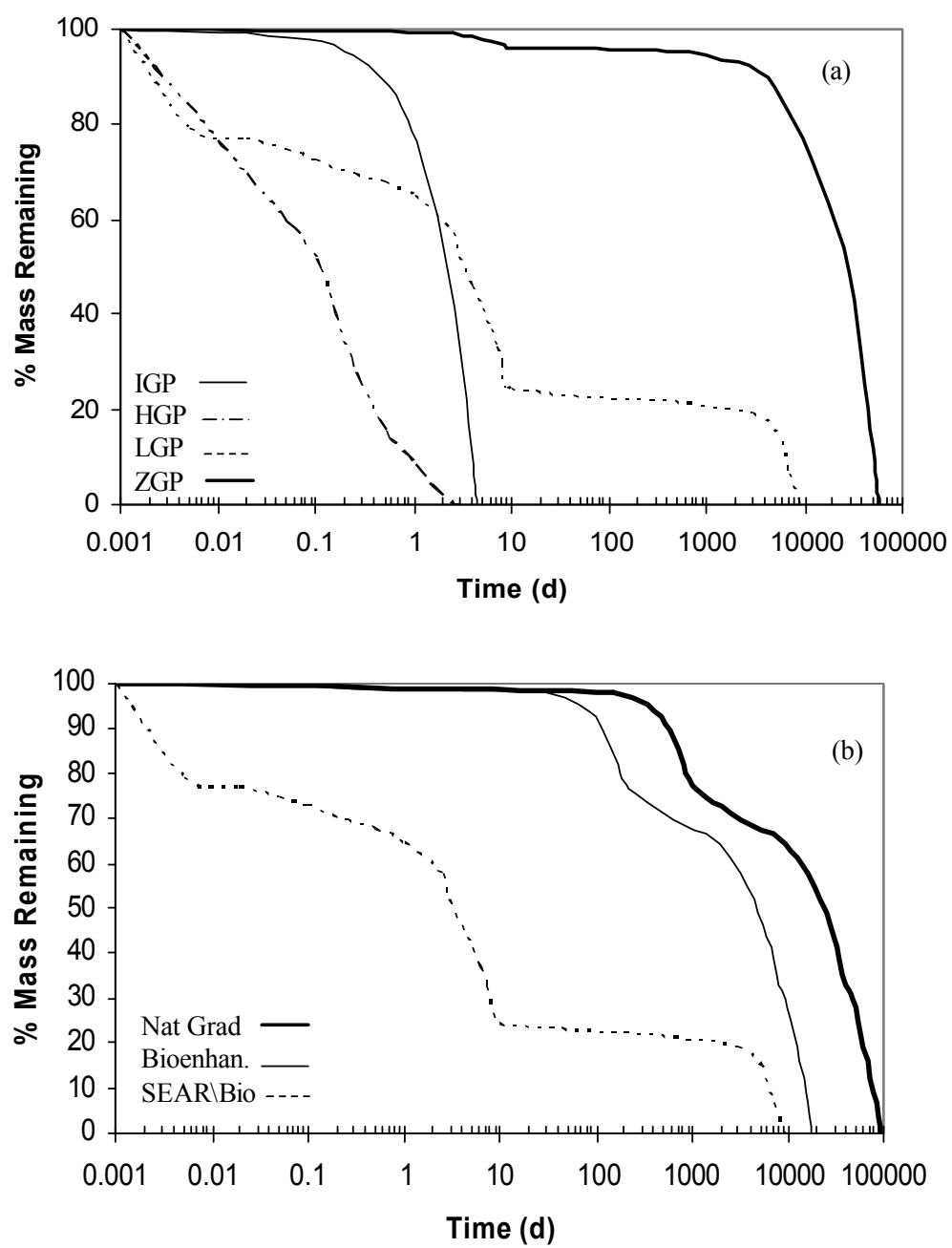








**Figure 5**



**Figure 6**